Supporting Information

Strong Influence of Weak hydrogen bonding on actinide-phosphonate complexation: Accurate predictions from DFT followed by experimental

validation

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Experimental

Materials and instruments

Phosphorus trichloride (Fluka), 1-pentanol, *iso*–pentanol, *sec*–pentanol (Merck), toluene and *n*– dodecane were obtained from Lancaster. ²³³U was purified by extraction in the form of uranyl nitrate from 4M nitric acid with 5% TBP/*n*– dodecane; this was followed by scrubbing with 4M nitric acid and stripping with dilute nitric acid. This procedure was adopted for separation of ²³³U from impurities and was used as tracer for uranium extraction studies. Am(III) solution was prepared by dissolving Am₂O₃ in concentrated HNO₃ (~16N) and diluting to the desired concentration. The plutonium solution in IV oxidation state was prepared by taking an appropriate quantity of Pu stock in 1M nitric acid. The oxidation state of Pu was maintained as Pu(IV)by the addition of 0.1mL of 2.5M NaNO₂ and Pu(IV)was extracted with 0.5M TTA/xylene. The organic phase containing Pu(IV)was scrubbed with 1M nitric acid and stripped with 8M nitric acid. The aqueous phase (strip solution) was washed twice with equal volume of *n*-hexane to remove the entrained organic phase. The stock solution was used for preparing aqueous Pu(IV) solutions for solvent extraction experiments. Nuclear grade thorium nitrate (Indian Rare Earths Ltd., Mumbai, India) was used as received without further purification.

¹H and ³¹P [¹H]–NMR spectra were recorded by BRUKER DMX–400 and all ¹H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 25°C, CDCl₃). H₃PO₄ was used as an external standard for ³¹P [¹H]–NMR.

Fourier-transform infra-red spectrometer model FTLA 2000 of ABB Bomem Inc., USA was used for recording IR spectrum of all organic extractants. The liquid samples were recorded on Zn-Se window in the spectral range of 4000-650 cm⁻¹ at a resolution of 4 cm⁻¹.

ESI MS analysis was carried out using an Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700. Optimized conditions were as follows: Ion spray Voltage 3.2 kV; Declustering Potential (DP) 50 V, Entrance Potential (EP) 10 V.

General procedure for the synthesis of H–phosphonates

One equivalent of phosphorous trichloride was dissolved in twice the volume of dichloromethane and stirred in a round bottom flask kept in an ice bath. Three equivalents of the appropriate alcohol (eg. 1–pentanol, iso–pentanol, sec–pentanol) diluted in two volumes of dichloromethane were added drop–wise to the cooled reaction flask. Once addition was complete, the reaction was stirred overnight and then quenched with an ice water mixture. Hydrochloric acid was a by–product, which was removed by washing with sodium carbonate until the wash water was basic. The aqueous and organic phases were subsequently separated using a separating funnel and the organic phase was thoroughly washed with water to remove excess carbonate and any other water soluble impurities. Sodium sulphate was added to the separated organic phase and left to stand in order to remove any moisture present in the organic phase. Finally the organic phase containing the product was placed in a rotary evaporator for three hours to remove the volatile solvent (dichloromethane) and other impurities. The reaction scheme is represented in Scheme 1.





Scheme S1: Preparation route for H-phosphonates from the starting materials phosphorous

Figure 1S: Proton NMR spectrum of Diamyl H phosphonate (DAHP)



Figure 2S: ³¹P NMR spectrum of Diamyl H phosphonate (DAHP).



Figure 3S: Proton NMR spectrum of Diisoamyl H phosphonate (DiAHP)





Figure 5S: Proton NMR spectrum of Disecamyl H phosphonate (DsAHP)



Figure 6S: ³¹P NMR spectrum of Disecamyl H phosphonate (DsBHP).

Physicochemical properties of H-phosphonates

Measurement of density

Density is an important parameter for a system to qualify as a suitable extractant for the solvent extraction process. The density difference between the aqueous and organic phase must be large enough in order to minimise phase separation time. Density of the synthesised extractants was measured using a 500μ L glass pipette. The density was calculated from the weight difference of the pipette before and after it was filled with the compound.

Measurement of viscosity

Viscosity of an extractant influences mass transfer between phases. It plays a vital role in predicting the nature of flow in any process. Measuring viscosity is useful in the calculation of the power requirements for the unit operations such as mixing, pipeline design and pump characteristics. Viscosity of a fluid can be determined by measuring the time of flow of a given volume of liquid through a vertical capillary under the influence of gravity:

$$\eta = \frac{\pi \Delta p t r^4}{8 l V}$$

Where η is the viscosity of the fluid, Δp is the difference in the pressure between two ends of the tube, *t* is the time for volume *V* to flow out, *r* is the radius of the capillary and *l* is the length of the capillary (31). With both ends of the viscometer tube open:

$$\eta = \frac{\pi h \rho g t r^4}{8 l V}$$

Where *h* is difference in height between the liquid levels in the two reservoirs used in the experiment, ρ is density of the liquid and *g* is acceleration due to gravity. For a given volume of liquid and a given viscometer

$$\eta = k\rho t$$

Where $k = \frac{\pi h g r^4}{8 l V}$

Additionally viscosity is related to the activation energy of liquid flow E_a , by the equation

$$\eta = Ae^{\frac{E_a}{RT}}$$

Where *A* is a constant, *T* is the temperature and *R* is the gas constant.

The viscosity of the extractants (DAHP, DiAHP and DsAHP) was measured by Oswald viscometer (32). A known volume (~ 15mL) of liquid was taken in the viscometer and the time taken by the liquid to flow through the marked region of the Oswald viscometer was measured. The driving pressure p at all stages of the flow of a liquid is given by $h\rho g$, where h is the difference in the heights of the liquid in upper and lower bulb, ρ the density of the liquid and g the acceleration due to gravity. The viscosity of fluids can be evaluated by the comparative method where one of the fluids is water whose density and viscosity as a function of temperature are well reported in the literature. The viscosity of the fluid of interest can be determined using the following expression.

$$\frac{\eta_e}{\eta_w} = \frac{\rho_e t_e}{\rho_w t_w}$$

Where η_e , ρ_e and t_e are the viscosity, density and time taken for the extractant to pass through the marked region of the viscometer of the fluid to be determined. η_w , ρ_w and t_w are the viscosity, the density and the time for the water system under identical conditions. Viscosity measurements were carried out for DAHP, DiAHP and DsAHP and the natural logarithm of viscosity was plotted against the inverse of temperature. Linear plots were obtained and from the slope of the graphs, activation energy was calculated as the slope of the graphs give *Ea/R*.

Measurement of aqueous solubility

An equal volume of extractant and distilled water were equilibrated in a glass equilibration tube for 8 hours. The two phases were transferred to a separating funnel and allowed to settle for 24 h. Once the phase separation was complete, the aqueous layer was carefully separated using a pipette and analysed for the total carbon content using Total Organic Carbon (TOC) analyser. The solubilities of the H–phosphonates were determined by this method.



Figure 7S: ESI-MS spectra for the DsAHP bare ligand denoted as (L). The peaks corresponding to the relevant m/z are assigned.



Figure 8S: ESI-MS spectra for the DsAHP bound uranyl nitrate complex denoted as (M). The peaks corresponding to the relevant m/z are assigned.



Figure 9S: ESI-MS spectra for the DsAHP bound thorium nitrate complex denoted as (M). The peaks corresponding to the relevant m/z are assigned.

Table 1S: Solvent corrected binding free energies (kcal mol⁻¹) using M06-2X and DFT-D3 functionals BP86 and the hybrid PBE0 functional of uranyl nitrate complexes with DAHP and DsAHP.

	Binding free energy (kcal/mol)		
Complex	M06-2X	BP86-D3BJ	PBE0-D3BJ
UO ₂ (NO ₃) ₂ ·2DAHP	-9.22	-27.78	-16.18
UO ₂ (NO ₃) ₂ ·2DsAHP	-13.41	-30.41	-19.03